Appendix A

Oxygen Supply in a Zinc-Air Cell

1. Introduction

The following sections describe some theories used for the CFD simulation of airflow and oxygen diffusion and convection through cathode can openings of a metal-air cell. Boundary conditions and assumptions are explained.

2. Conservation Equations

When a metal-air cell is in discharge, it consumes oxygen and forms zinc oxide. As the surrounding environment supplies oxygen, the total mass of the cell should increase. For fluid dynamics analysis, only the gas volume in the plenum between the can and the cathode is of interest, and this volume is considered to be constant. The gas inside the plenum will observe the law of mass conservation.

2.1 Mass conservation equation

The mass conservation equation has the form of [Fluent, 1998]

$$\frac{\partial \rho}{\partial t} + \rho \frac{\partial u_x}{\partial x} + \rho \frac{\partial u_y}{\partial y} + \rho \frac{\partial u_z}{\partial z} = 0$$

where ρ is density (g/cm^3), u_x , u_y and u_z are velocity components (cm/s) in the directions x, y and z, respectively.

2.2 Mass Conservation for Fluid with N Species

The mass conservation equation for one of the N species in a fluid is [Fluent, 1998]

$$\rho\left(\frac{\partial c_n}{\partial t} + u_x \frac{\partial c_n}{\partial x} + u_y \frac{\partial c_n}{\partial y} + u_z \frac{\partial c_n}{\partial z}\right) = -\frac{\partial j_{nx}}{\partial x} - \frac{\partial j_{ny}}{\partial y} - \frac{\partial j_{nz}}{\partial z} + q_{c_n}$$

where c_n is the concentration (in mass fraction) of species n (n = 1 … N), q_{cn} is a source term (g/cm^3·s), and j_n is the diffusive mass flux (g/cm^2·s) expressed by Fick's First Law of Diffusion [Crow, 1994], in the s (s = x, y, z) direction,

$$j_{nx} = -\rho D_n \frac{\partial c_n}{\partial s} \tag{2.1}$$

where D_n (or α_n in some literature) is the mass diffusion coefficient or diffusivity (cm^2/s) of species n.

2.3 Momentum Conservation

The Navier-Stokes form of the momentum equations in the s direction is [Zhang, 1986]

$$\rho\left(\frac{\partial u_s}{\partial t} + u_x \frac{\partial u_s}{\partial x} + u_y \frac{\partial u_s}{\partial y} + u_z \frac{\partial u_s}{\partial z}\right) = -\frac{\partial p}{\partial s} + \mu\left(\frac{\partial^2 u_s}{\partial x^2} + \frac{\partial^2 u_s}{\partial y^2} + \frac{\partial^2 u_s}{\partial z^2}\right) + \rho f_s$$

where μ is the dynamic viscosity, p is pressure, and f_x , f_y and f_z are the body forces per unit mass, in the directions x, y and z, respectively. For the analyses of gas transport, the effect of body forces can be omitted.

3. Equation of State

For an ideal gas, the equation of state is [Zhang, 1986]

$$\rho = \frac{Mp}{RT} \tag{3.1}$$

where M is the molecular weight of the gas, and R is the universal gas constant.

For an ideal mixture of gases with N species, there are

$$\frac{1}{M} = \sum_{n=1}^{N} \frac{c_n}{M_n}$$

and

$$\sum_{n=1}^{N} c_n = 1$$

The total density of the gas is

$$\rho = \rho_1 + \rho_2 + \cdots + \rho_N = \sum_{n=1}^{N} \rho_n$$

where $\rho_n = \rho c_n$ is the density (g/cm^3) of species n.

4. Partial Pressure

From the equation of state, equation (3.1), the total pressure is

$$p = \frac{RT\rho}{M} = RT\rho \sum_{n=1}^{N} \frac{c_n}{M_n} \qquad (4.1)$$

Let

$$p = \sum_{n=1}^{N} p_n$$

Then the partial pressure for species n is

$$p_n = \frac{RT\rho c_n}{M_n} = R_n T \rho_n \qquad (4.2)$$

where R_n is the gas constant for species n.

The change in partial pressure of a species in a gas reflects the difference of the species at different positions. A gas tends to reduce the difference in its contents and become uniform. Molecules of the species move from a place with high concentration towards a place with low concentration until the gas becomes uniform. This is the process of diffusion and is explained by Fick's First Law, i.e., equation (2.1), as written in the partial pressure

$$j_{ns} = -D_n \frac{M_n}{RT} \frac{\partial p_n}{\partial s}$$

This equation shows that the partial pressure acts like real pressure. The mass flux through a unit area during a unit time is proportional to the partial pressure gradient in the direction of the flux.

The volume of the plenum occupied by the gas between the cathode can and the cathode surface is V. The temperature is T. At time $t = 0$, the condition of the gas in the plenum is in its original state, i.e., the same as the ambient. From equation (3.1), there is

$$p_a = \frac{R_a T m_a}{V}$$

where p_a, R_a and m_a are the total pressure, gas constant and mass of the air in the plenum at $t = 0$, respectively. The total pressure can be expressed as the sum of partial pressures of oxygen and nitrogen. (Here, nitrogen includes the components of nitrogen and other gases except for oxygen.). Then, from equation (4.1), there is

$$p_a = p_{oa} + p_{na} = \frac{R_o T m_{oa}}{V} + \frac{R_n T m_{na}}{V} \tag{4.3}$$

5. Oxygen Consumption Rate

Suppose the consumption rate of oxygen in the cell is b (g/s), then the oxygen mass m_o (g) in the plenum equals the difference of the original m_{oa} and the consumed oxygen Δm_o:

$$m_o = m_{oa} - \Delta m_o = m_{oa} - b\Delta t \tag{5.1}$$

Referring to Faraday's First Law [Moore, 1972]

$$\Delta m_o = \frac{M_o}{zF} I \Delta t$$

where I is the cell current, z is charge number of electrons, and F is the Faraday constant.

The relation of oxygen consumption rate to the current is

$$b = \frac{\Delta m_o}{\Delta t} = \frac{M_o I}{zF} \tag{5.2}$$

Therefore, the oxygen mass from equation (5.1) becomes

$$m_o = m_{oa} - \frac{M_o I}{zF} \Delta t = \rho_a c_{oa} V - \frac{M_o I}{zF} \Delta t \tag{5.3}$$

6. Differential Pressure in a Metal-Air Cell

Differential pressure Δp is the driving force for convection. For a metal-air cell the differential pressure is the vacuum in the plenum created by the reduction process of the air electrode.

6.1 In a sealed cathode can

Consider a metal-air cell discharged in the sealed condition. At the time $t = \Delta t$, the total pressure in the plenum is, according to equation (4.1),

$$p = p_o + p_n = \frac{R_o T m_o}{V} + \frac{R_n T m_n}{V} \tag{6.1}$$

In the plenum, only oxygen is consumed. If there is no extra airflow into the plenum, then nitrogen mass $m_n = m_{na}$.

Using all the values known in equation (6.1), the differential pressure is

$$\Delta p = p_a - p = p_a(0.1896 - 0.7154\frac{m_o}{m_{na}}) \tag{6.2}$$

When all the oxygen inside is consumed, i.e., $m_o = 0$, the maximum vacuum that the cell may create is $\Delta p_{max} = 0.1896\, p_a$.

Substitute m_o in equation (6.2) with its relation to current, equation (5.3), then the differential pressure in relation with current I (mA) becomes

$$\Delta p = 5.932 \times 10^{-8} \frac{p_a I}{m_{na}} \Delta t = 63.12 \frac{I}{V} \Delta t$$

6.2 In a can with air-access ports

If the airflow rate through the air-access ports is Q_f (cm^3/s), the mass of air coming into the plenum is

$$\Delta m_f = \rho_a Q_f \Delta t$$

The partial pressure increase because of the mass increase in the plenum is, by applying equation (4.2),

$$\Delta p' = \frac{R_a T \Delta m_f}{V} = \frac{R_a T \rho_a Q_f}{V} \Delta t = \frac{p_a Q_f}{V} \Delta t$$

The total differential pressure is

$$\Delta p = (6.226 \times 10^{-5} I - Q_f)\frac{p_a}{V} \Delta t \tag{6.4}$$

The condition of this equation is $\Delta p \leq 0$. If $\Delta p = 0$, then

$$Q_{fmax} = 6.226 \times 10^{-5} I$$

This is the maximum airflow rate the current can generate on condition that there were no other forces such as pumping. The proportion of oxygen provided by convection to the total oxygen consumption is

$$\frac{\Delta m_{of}}{\Delta m_o} = \frac{\rho_a c_o z F}{M_o}\frac{Q_f}{I} = 3045\frac{Q_f}{I} = 0.1896$$

Thus, it is believed that the highest oxygen proportion from convection is 19%. The rest 81% of oxygen will be provided through diffusion. Although convection itself does not contribute much of the oxygen, its influence to the cell performance could be reflected by its effect on diffusion.

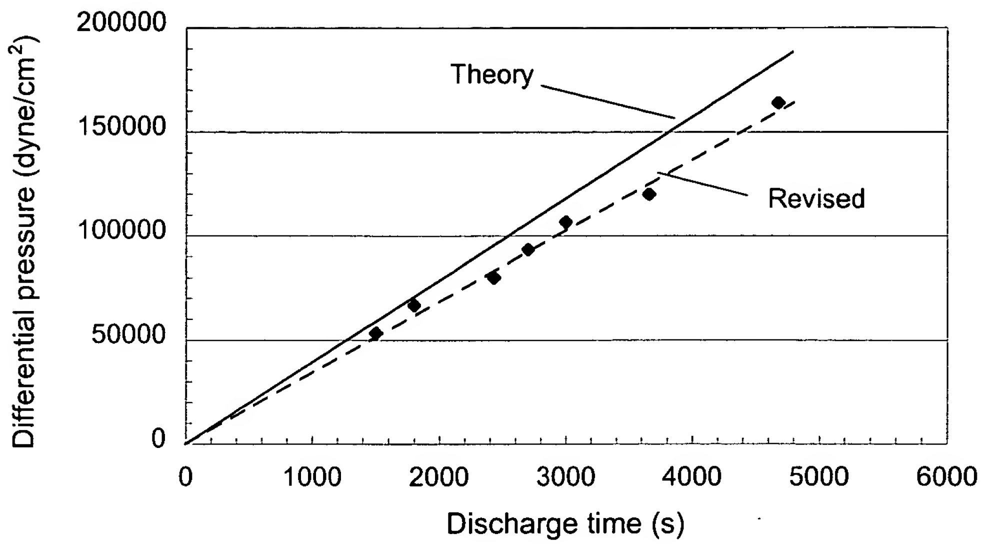
6.3 Comparison with test data

The following is an example to show the use of the theoretical analysis of the differential pressure with a set of test data published in the literature [Ohta, 1997]. The test was to measure the differential pressure changes of a test metal-air cell as electrochemical reduction of oxygen. The cell was partially sealed with a leakage of $Q_f = 9.3 \times 10^{-6}$ cm^3/s. The volume of the plenum was volume $V = 8.1$ cm^3. The constant discharge current of the cell was $I = 5.2$ mA.

The vacuum changes in the plenum with time is, using equation (6.4),

$$\Delta p = (6.226 \times 10^{-5} I - Q_f)\frac{p_a}{V}\Delta t = 39.34\ \Delta t$$

The chart below shows the comparison of the theoretical analysis and the test. There are some discrepancies and the difference increases with time. Consider that the maximum vacuum a metal-air cell can produce is about 192000 dyne/cm^2 and the theoretical value at the end of test nearly reaches the maximum. This may mean that either the test cell could not keep the current because of low oxygen concentration or the leakage was increased because of higher differential pressure.



A revised form of the differential pressure change can be written to correlate the test data, which is $\Delta p = 34.25\ \Delta t$ and it is shown by the dotted line in the chart.

7. Conclusions

The following are some assumptions and boundary conditions concluded from the theories of fluid dynamics of the air management of a metal-air cell to be used in the CFD simulation.

1. The use of oxygen in a metal-air cell creates a vacuum pressure in the cathode plenum. This vacuum draws air into the plenum through the air-access openings.
2. There is a convection flow of air that provides the cell with less than 19% of the total oxygen it uses.
3. Over 81% oxygen comes from diffusion.
4. The oxygen consumption rate of a metal-air cell per mA current is 8.291×10^{-8} g/s.
5. The maximum vacuum a metal-air cell may get in the cathode plenum is about 192000 dyne/cm^2 or 0.192 atm.
6. The maximum airflow rate that a metal-air cell could may create per mA current is 6.226×10^{-5} cm^3/s.

It is assumed that the cathode surface is flat and uniform and that it can consume the oxygen that reaches its surface. Therefore, the CFD simulation does not consider the variations in the cathode properties.

References

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